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Lignosulfonate-Modified Calcium Hydroxide for Sulfur Dioxide Control

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16. ABSTRACT The article discusses the use of lignosulfonate-modified calcium hydroxide--Ca(OH)2--for sulfur dioxide (SO2) control. The limestone injection multistage burner (LIMB) process is currently being developed at the U.S. EPA as a low cost retrofittable technology for controlling oxides of sulfur and nitrogen from coal-burning utility boilers. The most effective commercial calcium-based sorbent for this process is Ca(OH)2, with SO2 removals of about 50%. Additions of calcium lignosulfonate up to 1.5 mass % of the dry product, introduced with the water of hydration, increase the SO2 capture of the resulting Ca(OH)2 to 60%. This is achieved through particle size reduction in the modified hydroxides. The principal mechanism of size reduction appears to be deagglomeration of the Ca(OH)2 crystals; a secondary benefit is derived from crystal size reduction.

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Sulfur Dioxide	Stationary Sources	07B
Calcium Hydroxides	Lignosulfonates	
Lignocellulose	Limestone Injection Multistage Burners (LIMB)	06A
Coal		21D
Combustion		21B
Calcium Carbonates		

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Lignosulfonate-Modified Calcium Hydroxide for Sulfur Dioxide Control

The limestone injection multistage burner (LIMB) process is currently being developed at the Environmental Protection Agency as a low-cost, retrofittable technology for controlling oxides of sulfur and nitrogen from coal-burning utility boilers. The most effective commercial, calcium-based sorbent for this process is calcium hydroxide [$Ca(OH)_2$], which achieves sulfur dioxide (SO_2) removals of around 50% at a calcium-to-sulfur ratio of 2. Additions of calcium lignosulfonate up to 1.5 mass % dry product, introduced with the water of hydration, increase the SO_2 capture of the resulting $Ca(OH)_2$ to 60%. This is achieved through particle size reduction in the modified hydroxides. The principal mechanism of size reduction appears to be through deagglomeration of the $Ca(OH)_2$ crystals, while a secondary benefit may be derived from crystal size reduction.

Background

The limestone injection multistage burner (LIMB) process being developed by the Environmental Protection Agency is a low-cost, retrofittable technology for controlling oxides of sulfur and nitrogen from coal-fired utility boilers. Sulfur dioxide control is achieved by injection of a calcium-based sorbent into the boiler, while nitrogen oxides are reduced by delaying the mixing of fuel and air through the multistage burner. The large population of older boilers, for which the expense of flue gas desulfurization systems cannot be justified, is the primary market.

A lengthy testing program has shown that injection of sorbent at temperatures no higher than 1230 °C is most favorable, presumably due to the avoidance of sintering. It has also shown that, of the commercially available calcium-based materials which can be used as sorbents, $Ca(OH)_2$ is the most effective in capturing SO_2 (Overmoe et al., 1985; Beittel et al., 1985; Bortz and Flament, 1985; Slaughter et al., 1985). At a calcium-to-sulfur ratio of 2, commercial $Ca(OH)_2$ appears to be capable of removing about 50% of the SO_2. This still falls short of the 60% removal goal for the LIMB process, however.

It has been established that sulfur capture by sorbent in a high-temperature furnace environment occurs via sequential steps: (1) diffusion of SO_2 from the bulk gas to the particle surface; (2) diffusion of SO_2 through the porous lime to the particle interior; (3) diffusion of the reactant sulfur species through the reaction product layer; and (4) heterogeneous reaction at the CaO/calcium sulfate ($CaSO_4$) interface (Cole et al., 1986). The same study shows that surface area loss due to pore closure and product layer buildup is the limiting factor in the overall

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Table I. Elemental Analysis of Presque Isle Limestone

component	ppm	component	ppm
Ca	365 000	Mn	145
Mg	6 540	S	
Si	3 860	K	
Al	418	Na	147
Fe	1 550		

reaction sequence. Approximately 60% of the surface area becomes unavailable for reaction with SO_2 in the first 100 ms of the reaction.

One method of increasing sorbent utilization, and therefore capture of SO_2, is to decrease the particle size of the sorbent (McCarthy et al., 1986; Borgwardt and Bruce, 1986; Cole et al., 1986), in this case $Ca(OH)_2$. In this fashion the diffusion pathways are shortened and higher utilizations achieved before product layer buildup terminates the reaction. Typical commercial hydroxides have measured mass median diameters of 2–7 μm, with 50% of the material often being considerably larger. The larger particle sizes are a result of either or both of two factors: (1) the crystal size of the $Ca(OH)_2$ initially produced during the hydration of CaO by water and/or (2) the agglomeration of $Ca(OH)_2$ crystals due to hydrogen bonding between their absorbed water layers. The objective of this study was to identify additives which can be used in the water of hydration to reduce the particle size of commercial $Ca(OH)_2$ by either of these mechanisms.

Experimental Section

Materials. The parent material used in this study is a commercially available Michigan limestone from the Presque Isle quarry. Table I shows the chemical analysis of the stone. It was chosen because it is currently used by several lime companies and because it displays no chemical or physical qualities to suggest that it is in any way exceptional.

The additive chosen is calcium lignosulfonate which is available as a dry powder under the tradename of Lignosite from the Georgia Pacific Corporation. The material is discussed by Grayson (1983) under the category of anionic surfactants.

Calcination and Hydration. Presque Isle limestone crushed and screened to −595 μm was calcined to CaO at 1000 °C for 16 h in a Lindberg muffle furnace under a nitrogen flow of 6 L/min.

Hydration was conducted in a laboratory-scale hydrator consisting of a 400-mL Pyrex beaker suspended in a constant temperature bath maintained at 100 °C. A mechanically propelled stirrer was used to mix the water and lime. Each hydration was conducted by loading 10 g of dry lime into the hydrator and allowing the lime to achieve thermal equilibrium in the bath. The stirrer was started, and a single, rapid addition of 100 °C water was syringed into the hydrator in the molar ratio of $H_2O/CaO = 2.6$. After 15 min, the hydration vessel was purged of remaining water vapor with nitrogen, leaving a thoroughly dry product. Modified hydrates were produced by dissolving sufficient calcium lignosulfonate in the hydration water to yield 0%, 0.5%, 1.0%, 1.5%, 2.0%, 3.0%, and 4.0% on a mass basis of lignosulfonate in the product $Ca(OH)_2$.

Sulfation. Reactivity of the hydrates with SO_2 was determined by using the flow reactor illustrated in Figure 1 and described elsewhere (Kirchgessner et al., 1986). The reactor is operated at a nominal temperature of 1000 °C, and sorbent residence time is 1 s. Flow rates of the constituent gases at standard temperature and pressure are

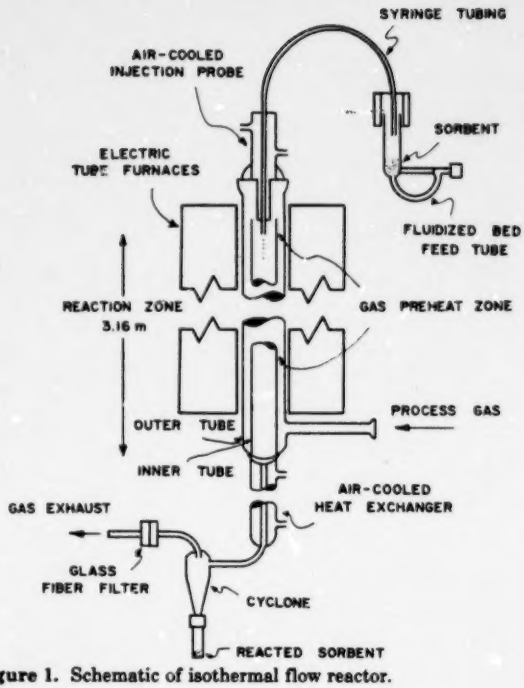

Figure 1. Schematic of isothermal flow reactor.

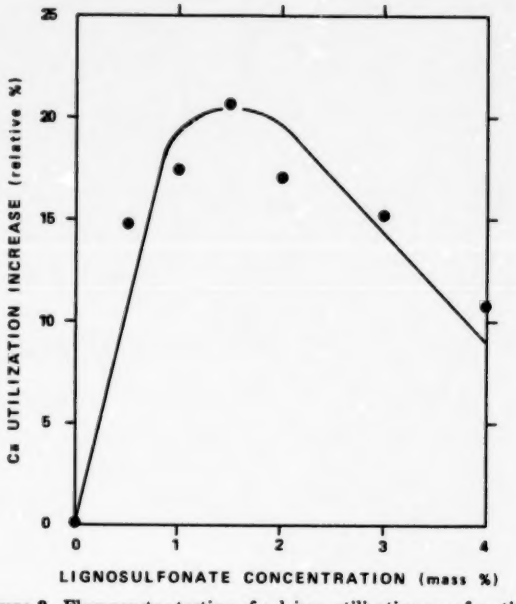

Figure 2. Flow reactor testing of calcium utilization as a function of calcium lignosulfonate content in hydrate.

N_2, 6.19 L/min; air, 1.94 L/min; and SO_2, 0.025 L/min (3000 ppm). Sorbent samples are injected at rates low enough to maintain differential conditions with respect to SO_2. Calcium utilization of reactor products is calculated after analyses for calcium by atomic absorption spectrophotometry and for sulfate by ion chromatography. No other sulfur species have been detected.

Results and Discussion

The results of sulfation testing in the flow reactor are shown in Figure 2. It displays the percent increase in calcium utilization for lignosulfonate-modified hydrates

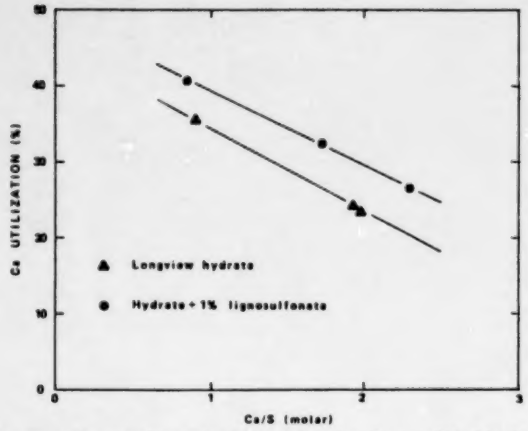

Figure 3. Reactivity testing of a modified and unmodified hydrate in a 1×10^6 Btu combustor.

relative to the unmodified hydrate, which is plotted at the origin. At the optimal lignosulfonate concentration of 1.5%, a 20% relative increase in calcium utilization is achieved. The actual calcium utilizations were 25% for the unmodified hydrate and 30% for the hydrate modified with 1.5% lignosulfonate. At a Ca/S ratio of 2, which would probably be used during boiler injection of sorbent, the equivalent sulfur captures would be 50% and 60%, respectively.

In a parallel experiment at Southern Research Institute, a commercial Longview CaO was hydrated without additives and with 1% calcium lignosulfonate. The resulting sorbents were tested for reactivity in a 1×10^6 Btu coal-fired combustor at an average temperature of 1250 °C. As shown in Figure 3, calcium utilizations obtained at a Ca/S ratio of 2 are nearly identical with those obtained in the isothermal flow reactor. This demonstrates the potential applicability of the sorbent modification technique to other parent materials, different combustor scales, and, of primary importance, when using coal as the fuel.

It was assumed that the additive would reduce the particle size of $Ca(OH)_2$ in either or both of two ways: (1) by reducing the primary crystal size of the material as it formed in the hydration process; (2) by preventing agglomeration of the hydrate particles after they had formed. The first effect would be achieved by reduction of surface energy at the nucleus/solution interface during hydration and an increase in the nucleation rate resulting in smaller crystals. The second effect would be produced through the introduction of a hydrophobic material and the prevention of hydrogen bonding between adjacent adsorbed water layers.

To determine which, if either, of the two mechanisms listed was responsible for the increase in calcium utilization, size analyses of the sorbents were conducted by two methods. One method determined the aerodynamic size distribution using the fluidized bed sorbent feed system from the flow reactor in conjunction with Gelman cascade impactors. It was believed that this system would accurately measure the size range of materials normally available for sulfation in the reactor and that these materials would consist of various sized agglomerates of crystals. The second method of sizing was by Sedigraph, a sedimentation technique conducted in a liquid medium containing a dispersant. This method would more closely approximate the size distribution of the individual $Ca(OH)_2$ crystals.

Figure 4 shows the results of size analyses by cascade impactor as a function of calcium lignosulfonate content.

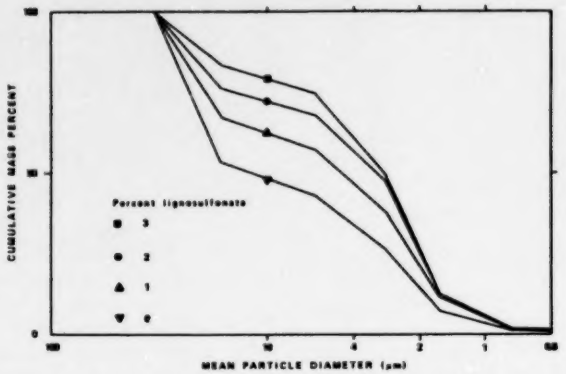

Figure 4. Size analyses of modified and unmodified hydrates by cascade impactor.

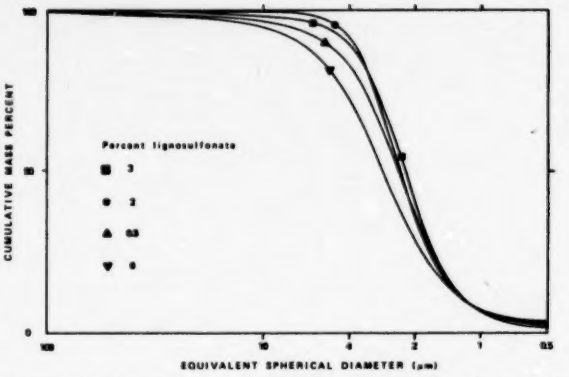

Figure 5. Size analyses of modified and unmodified hydrates by Sedigraph.

Mass median diameters range from 12 μm for the unmodified hydrate to 3 μm for the hydrate containing 3% lignosulfonate. The distributions themselves show even more dramatically the diminishing particle size with increasing lignosulfonate content. It seems reasonable to conclude from these analyses that the additive has been highly effective in disaggregating the agglomerates caused by hydrogen bonding in the adsorbed water layers around the individual hydrate crystals. It is hypothesized that these bonds are prevented from forming by the incorporation of the lignosulfonate molecule into the adsorbed water layer and, in particular, to the presence of the organic, hydrophobic portion of the molecule.

Figure 5 shows the size distributions determined by the Sedigraph technique, again as a function of lignosulfonate content. In this case all samples are represented by finer size distributions than were determined by cascade impactor. This was expected as a result of the dispersive nature of the technique. Even within this relatively small range of size distributions, however, the mass median diameters range from 2.9 μm for the unmodified hydrate down to 2.2 μm for the hydrate containing 3% calcium lignosulfonate. Again the entire distribution shows a more impressive change than is reflected by the mass median diameter alone. It is interesting to note that the mass median diameter for the hydrate containing 3% lignosulfonate is similar when measured either by cascade impactor or by Sedigraph, suggesting that this level of additive almost completely deagglomerates the sorbent into its component crystals. Sedigraph results suggest that a small decrease in hydrate crystal size has occurred as predicted.

If particle size reduction were the only factor to be considered, one would expect the observed increases in calcium utilization to continue through the entire range of lignosulfonate additions. Calcium utilization peaks at the 1.5% lignosulfonate level, however, and decreases through the remainder of the range. It is suggested that, above the optimal level of 1.5%, the large lignosulfonate molecule (molecular weight of about 8000) or its residue may block access of the SO_2 molecule to reactive CaO sites.

Conclusions

It has been shown that modest amounts of calcium lignosulfonate (up to 1.5 mass % dry product), when added to the water of hydration, produce $Ca(OH)_2$, which demonstrates enhanced reactivities with SO_2 of up to 20% relative during furnace injection. This increased reactivity is attributed to particle size reduction achieved primarily through deagglomeration and secondarily through crystal size reduction. The fact that calcium utilization does not increase through the range of particle size reductions suggests that the large lignosulfonate molecule or its residue, when present in sufficient quantities, is capable of blocking access to reactive CaO sites by SO_2.

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Registry No. Calcium lignosulfate, 8061-52-7; SO_2, 7446-09-5; $Ca(OH)_2$, 1305-62-0.

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